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Supporting Information for

Vapochromic dye/graphene coated long-period fiber grating for benzene vapor sensing

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Experimental

Materials and methods

Dialdehyde-substituted Indacenodithiophene (IDT-2CHO) was purchased from Derthon Optoelectronic Materials Science Technology Co LTD (Shenzhen, China). CF_3-Ph-TCF was synthesized according to the reported procedure. ^{1}H NMR and ^{13}C NMR spectra were determined by Advance Bruker (600 MHz) NMR spectrometer. The HRMS spectra were analyzed on the Q-Exactive instrument. UV–Vis spectra were obtained using a Shimadzu 2600 spectrometer. The optimized geometry was evaluated by DFT calculations using Gaussian 09 at the hybrid B3LYP level by employing the split valence 6–31g(d) basis set.

Synthesis of IDT dye

IDT-2CHO (100 mg, 0.093 mmol) and CF_3-Ph-TCF (74 mg, 0.232 mmol) were dissolved in 5 mL $CHCl_3$, and the reaction mixture was stirred under reflux. After the reaction completed, the solvent was removed and the crude product was purified through silica-gel column chromatography, and the final product was obtained as dark green powder (110mg, yield: 70.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 15.5 Hz, 2H), 7.60 – 7.43 (m, 14H), 7.12(d, J = 9.0 Hz, 8H), 7.09 (d, J = 9.0 Hz, 8H), 6.70 (d, J = 15.4 Hz, 2H), 2.56 (t, J = 7.6 Hz, 8H), 1.39 – 1.13 (m, 32H), 0.86 (t, J = 6.4 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.72, 162.31, 155.44, 151.60, 147.41, 144.27, 142.71, 142.70, 142.64, 141.98, 140.70, 138.62, 136.84, 131.79, 129.92, 129.30, 128.88, 127.71, 127.70, 126.97, 118.31, 112.42, 110.60, 110.31, 110.22, 99.33, 63.02, 59.74, 35.57, 31.67, 31.23, 29.15, 22.57, 14.08. HRMS: m/z calcd for [M+Na] $^+$ $C_{102}H_{86}F_6N_6NaO_2S_4$: 1691.5492, found: 1691.5519.

Fabrication of long-period fiber grating

The single-mode fiber core has a refractive index of 1.452 and a radius of 4.1 microns; the cladding has a radius of 62.5 microns and a refractive index of 1.444. The optical fiber grating is designed with a period of 320 microns. The single-mode fiber is connected to an input (C+L) broadband light source and to an output spectrum analyzer (OSA) to record the spectral changes during the grating fabrication. The high-frequency CO_2 laser is computer-controlled and periodically scans the fiber along the transverse direction, which causes a periodic change in the refractive index of the fiber and creates a grating structure.

Graphene transfer and IDTC1 coating

The copper foil with graphene is cut to a suitable size and put into a copper etching solution to dissolve the copper foil substrate. The etching solution used in this experiment is a mixture of nitric acid, hydrochloric acid and copper nitrate. After the etching solution has completely etched the copper substrate, a transparent film will appear on the surface of the etching solution, which is the single-layer graphene-PMMA flexible protective layer. After that, the graphene-PMMA film is transferred to DIO water. The transfer is repeated several times in DIO water to ensure that the residual etchant on the graphene-PMMA flexible film is washed away. Subsequently, the long-period grating was placed into the DIO water and placed close to the graphene-PMMA flexible film, and the grating was used to carefully retrieve the graphene-PMMA flexible film from the water. After the graphene was successfully transferred to the long-period grating, the device is dried overnight. Then the graphene attached to the long-period grating is placed in acetone solution to dissolve PMMA. To this end, the graphene-coated long-period fiber grating is facilitated. For the dye coating, graphene-coated LPFG is immersed in the solution of CH_2Cl_2 containing IDTC1 (2×10^{-4} mol/L). The solution is kept still until the solvent is evaporated. Then the device is dried in vacuum for 24 hours for further sensing experiments.

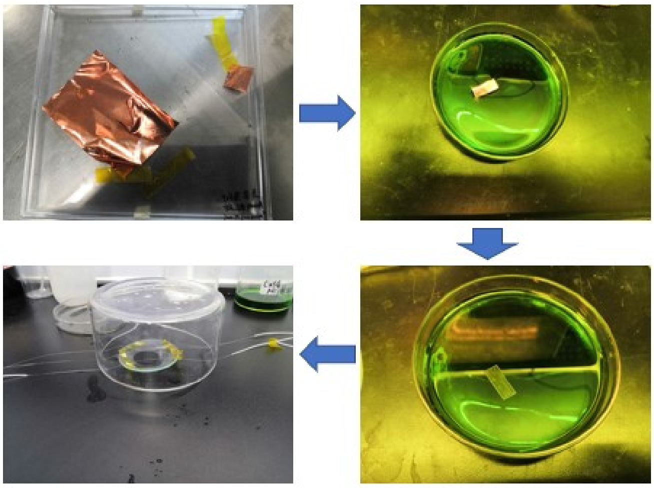

Figure S1 Schematically illustration of graphene transfer from copper substrate to optical fiber.

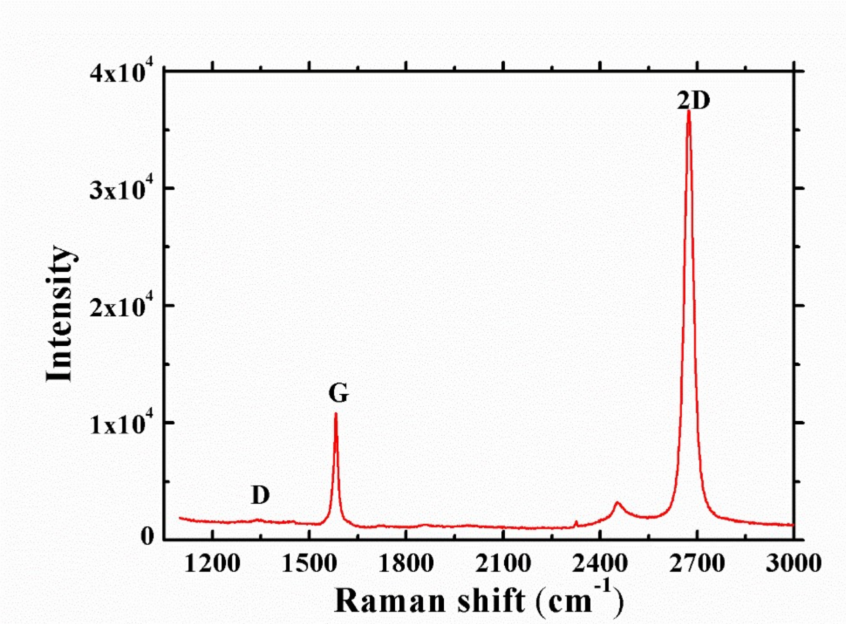

Figure S2 Raman spectrum of the transferred single-layer graphene on SiO_2 substrate.

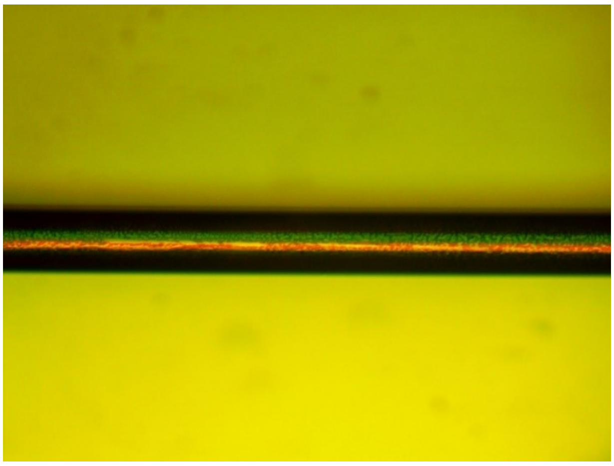

Figure S3 Optical microscopic image (x 10) of optical fiber with IDTC1 coated by drop-casting.

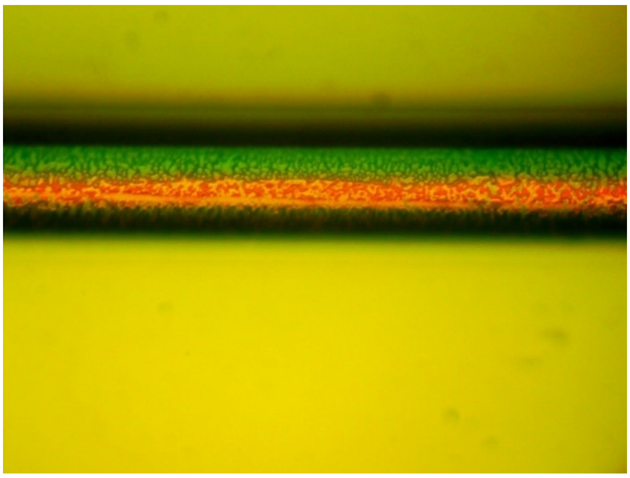

Figure S4 Optical microscopic image (x 20) of optical fiber with IDTC1 coated by drop-casting.

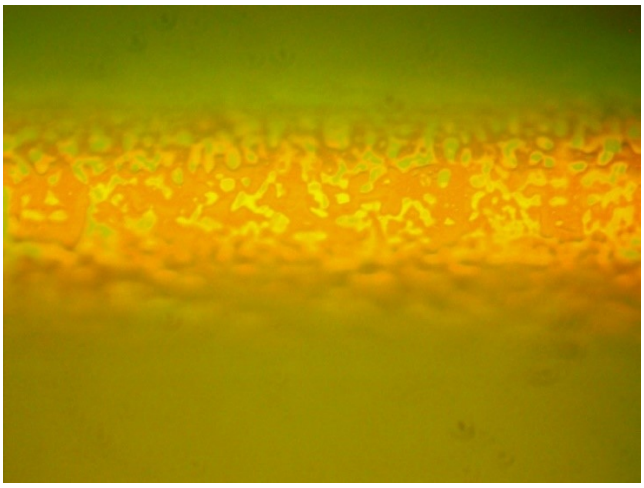

Figure S5 Optical microscopic image (x 50) of optical fiber with IDTC1 coated by drop-casting.

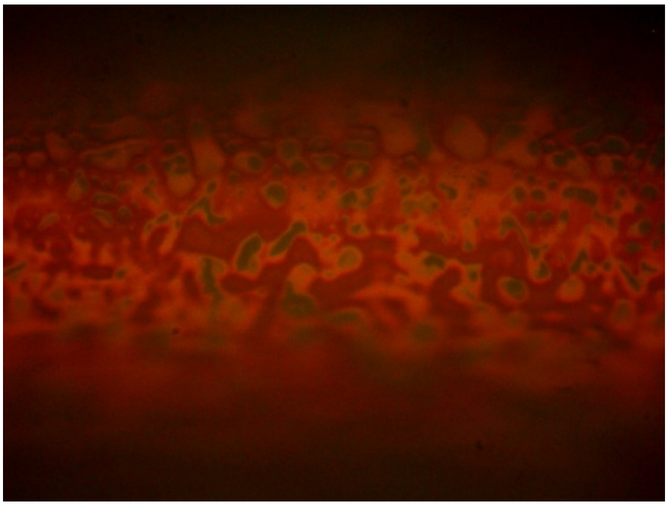

Figure S6 Optical microscopic image (x 100) of optical fiber with IDTC1 coated by drop-casting.